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Oxovanadium(IV) complexes with Schiff base : Synthesis, Characterization and Antifungal Studies

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ABSTRACT

A series of oxovanadium(IV) complexes have been synthesised with tetradentate Schiff base ligands derived by the condensation of benzoylacetone with amino acids, in which vanadyl ion shows kinetic template effect. The tentative structures of the vanadyl complexes have been proposed on the basis of FTIR, ESR, electronic spectra, elemental analysis and magnetic moment measurement. The oxidation state of oxovanadium(IV) with d^1 configuration is confirmed by ESR spectroscopy. All the complexes are screened against the fungi *Aspergillus flavus* and *Candida glaberata* which are found to be moderate antifungal agent.

Keywords: Schiff base, Benzoylacetone, Template effect, Antifungal agent.

1. INTRODUCTION

In recent years, the complexes of oxovanadium(IV) have received considerable attention because numerous studies have demonstrated that they possess insulin enhancing effects and can prevent the symptoms of diabetes in a variety of animal models[1-4]. Various oxovanadium(IV) complexes were subsequently developed, in which the organic ligands may provide ways for tuning the chemistry and bioactivities of vanadium, thereby minimizing the adverse effects without sacrificing important benefits[5-6]. Vanadium is a biometal in the first transition series which is important for animals, plants and microorganisms. The oxovanadium(IV) complexes act as catalyst in some biological processes[7,8] as well as in industrial processes[7-11]. The vanadium compounds have significant antifungal and antibacterial activities. The coordination chemistry of vanadium is an interesting area of current research because exact role of

vanadium in biological system is yet to be known. In view of this, we synthesised, characterised and carried out antifungal studies on a series of oxovanadium(IV) complexes with tetradentate Schiff base ligands derived by the condensation of benzoylacetone with amino acids such as glycine, alanine, serine, cysteine and valine as presented in this paper.

2. EXPERIMENTAL

2.1. Materials and Methods

Analytical grade chemicals and solvents were used without further purification. benzoylacetone was Aldrich product. All the Oxovanadium(IV) complexes were synthesised by standard in-situ method using $VOSO_4.3H_2O$ as metal salt.

2.2. Analytical Methods and Physical Measurements

Infrared spectra of the complexes were recorded in KBr medium in the range 4000 – 667 cm^{-1} on a Perkin-Elmer Paragon 1000 Fourier-transform spectrometer. The room temperature ESR spectra were recorded at IIT Guwahati and in frozen solution at SAIF, IIT Mumbai. The analysis of carbon, nitrogen and hydrogen were carried out at Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Bombay.

Sulphur was estimated gravimetrically as Barium Sulphate[12]. Vanadium was analysed in digested sample of vanadium(IV) complex using volumetric analysis based on redox reaction involving iodometry[13].

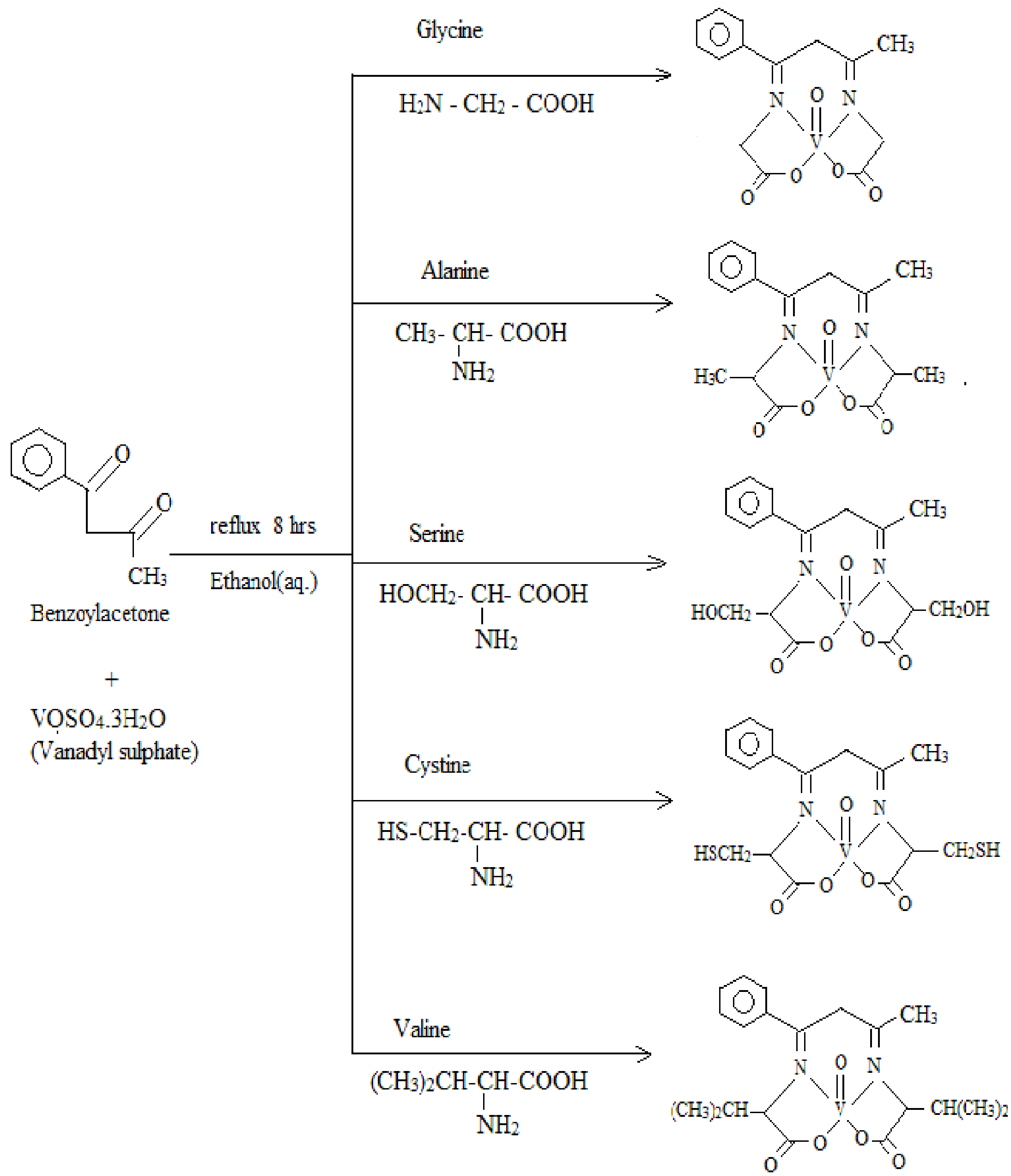
2.3. Preparation of oxovanadium(IV) complexes

The $VOSO_4.3H_2O$ (2mmol) dissolved in methanol (25mL) was added to refluxing solution mixture(1:1) of benzoylacetone (2mmol) and glycine (4mmol) in ethanol (20 mL) and the mixture was refluxed for 8 hours, when the colour of the solution turned green. The complex was precipitated by adjusting the pH. The solvent was removed under vacuo at room temperature and the light green colour product was isolated. The complex was thoroughly washed with 1:1 mixture of methanol and ethanol.

Same method was adopted to obtain oxovanadium (IV) complexes with ligand derived by condensation of benzoylacetone with alanine, serine, cysteine and valine.

3. RESULTS AND DISCUSSION

The oxovanadium (IV) complexes were sythesized using in-situ method by refluxing the reaction mixture of benzoylacetone and glycine or alanine or serine or cysteine or valine and vanadylsulphate in 1:2:1 molar ratio in aqueous methanol-ethanol mixture and the reaction proceeds as the scheme 1 shown in figure. The physical and analytical data of the complexes are presented in Table 1.



Scheme 1

Table 1 : Physical and analytical data of the complexes

Complex	Empirical formula	m.p. (^{0}C)	C% (cal.) found	H % (cal.) found	N% (cal.) found	O % (cal.) found	S% (cal.) found	V% (cal.) found
$[VO(L^1)]$	$VC_{14}H_{14}O_5N_2$	279	49.27 (49.31)	4.11 (4.12)	8.21 (8.23)	23.46 -	-	14.91 (14.95)
$[VO(L^2)]$	$VC_{16}H_{18}O_5N_2$	298	52.04 (52.07)	4.88 (5.00)	7.59 (7.60)	21.68 -	-	13.81 (13.80)
$[VO(L^3)]$	$VC_{16}H_{18}N_2O_7$	276	47.89 (47.96)	4.49 (4.52)	6.98 (6.99)	27.93 -	-	12.70 (12.73)
$[VO(L^4)]$	$VC_{16}H_{18}N_2O_5S_2$	281	44.35 (44.40)	4.15 (4.21)	6.46 (6.45)	18.49 -	19.47 (19.49)	11.76 (11.77)
$[VO(L^5)]$	$VC_{20}H_{26}N_2O_5$	285	56.48 (56.56)	6.11 (6.12)	6.59 (6.61))	18.82 -	-	11.98 (12.00)

Where

L^1 = Ligand obtained by the condensation of benzoylacetone and Glycine (molar ratio1:2)

L^2 = Ligand obtained by the condensation of benzoylacetone and Alanine (molar ratio 1:2)

L^3 = Ligand obtained by the condensation of benzoylacetone and Serine (molar ratio 1:2)

L^4 = Ligand obtained by the condensation of benzoylacetone and Cystine (molar ratio 1:2)

L^5 = Ligand obtained by the condensation of benzoylacetone and Valine (molar ratio 1:2)

3.1. Antifungal test

Well diffusion method[14] was used for the antifungal test of the oxovanadium(IV) complexes. The antifungal results of the synthesised complexes are recorded in Table 2. All the complexes showed significant antifungal activity against the fungi *Aspergillus flavus* and *Candida glaberata*.

Table 2 : Antifungal Activity of oxovanadium(IV) complexes

Complex	Antifungal Activity (% inhibition)	
	Aspergillus flavus	Candida glaberata
$[VO(L^1)]$	57	59
$[VO(L^2)]$	62	55
$[VO(L^3)]$	67	59
$[VO(L^4)]$	69	72
$[VO(L^5)]$	55	57
Standard[a]	100	-
Standard[b]	-	100

Amphotericin B[a], Miconazole[b]

3.2. Infrared Spectra

In the spectra of all the oxovanadium(IV) complexes, the ν(C=O) band intensity decreases significantly as compared to the free ligands and new bands appear at 1660, 1667, 1669, 1675 cm^{-1}. This observed down field shifts in complexes compared to the free Schiff base ligands suggest coordination of the carbonyl group to the metal. and also involvement of azomethine nitrogen[15]. A band at 308 cm^{-1}, further support the ν(V- N) vibration[16]. One more band at about 980-990cm^{-1} observed in all vanadyl complexes is assigned to the ν(V=O) vibration[17-19]. The bands at 1620 cm^{-1} indicates the presence of coordinated ν(C=N) band supporting the evidences for condensation of – NH_2 group of amino acids with the keto groups of benzoylacetone.

The ν_{asym} (COO^-) and ν_{sym} (COO^-) streching vibration of – COOH group in free amino acids are observed at ca. 1535 cm^{-1} and 1420 cm^{-1} respectively, giving $\Delta(COO^-)$ value of the order of 115 cm^{-1}. The respective ν_{asym} (COO^-) and ν_{sym}(COO^-) in case of oxovanadium(IV) complexes occurs at ca. 1565 cm^{-1} and 1430cm^{-1}, giving $\Delta(COO^-)$ value at 135 cm^{-1}, which is higher than the free amino acids. Such increase in the $\Delta(COO^-)$ values support the monodentate coordination of the amino acids via carboxyl group[20]. Thus, these observations indicate that the monovalent anionic species of the amino acids are coordinated to the oxovanadium(IV) centre.

3.3. Magnetic moment

The oxovanadium(IV) complexes show magnetic moment values in the range 1.72- 1.76 B.M. at room temperature and these values are in good agreement with oxovanadium(IV) complexes with one unpaired electron.

3.4. Electronic absorption spectra

The electronic spectral bands in the region 11490 cm^{-1} – 11810 cm^{-1}, 15109 cm^{-1}– 15856 cm^{-1} and 21205 cm^{-1} – 22501 cm^{-1}

are considered to correspond to the electronic transitions $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ as reported in the literature[21]. One more band is observed in the region 35210 cm^{-1} to 35709 cm^{-1} due to the electronic transition of azomethine linkage[22].

3.5. Electron spin resonance spectra

EPR is a useful tool in investigating the oxidation state of oxovanadium(IV) complexes [23]. At room temperature and at liquid nitrogen temperature, oxovanadium(IV) complexes show eight ESR bands which are due to hyperfine splitting arising from the interaction of the $3d^1$ - unpaired electron with a ^{51}V nucleus having I = 7/2 being the nuclear spin number[24]. Due to the rapid motion of molecules in solution at room temperature, the anisotropy is not observed and only g-average values were worked out at room temperature. Anisotropy[25] is clearly visible at liquid nitrogen temperature spectra and eight bands due to $g_{\|}$ and $g_{\perp}$ are observed . The $g_{\|}$, $g_{\perp}$, $A_{\|}$, $A_{\perp}$ values are measured from the spectra and given in table 3 which are in good agreement for oxovanadium(IV) complexes indicating single electron[26] in d-orbital of oxocation, VO^{2+}.

Table 3 : Room temperature g-values and liquid nitrogen temperature g and A values of the oxovanadium(IV) complexes.

Complex	Room temp.	Liquid nitrogen temperature					
	$\lvert g \rvert$	$g_{\|}$	$g_{\perp}$	$\lvert g \rvert$	$A_{\|}$	$A_{\perp}$	$\lvert A \rvert$
$[VO(L^1)]$	1.979	1.932	1.969	1.956	190.62	66.62	107.95
$[VO(L^2)]$	1.981	1.933	1.975	1.961	190.65	65.84	107.44
$[VO(L^3)]$	1.979	1.935	1.974	1.961	190.91	65.77	107.48
$[VO(L^4)]$	1.981	1.937	1.972	1.960	190.82	65.79	107.46
$[VO(L^5)]$	1.983	1.930	1.975	1.960	190.86	65.82	107.50

The above analytical and spectral data support the tentative structures of oxovanadium (IV) complexes as shown in the scheme 1.

4. CONCLUSION

A series of novel oxovanadium(IV) complexes were synthesized and characterized. The spectral data show that oxovanadium(IV) cation has significant kinetic template effect with Schiff base ligands derived by condensation of benzoylacetone with aminoacids. The Schiff base tetradentate ligands are bonded with VO^{2+} cation through the azomethine nitrogen atoms and o-donor atoms of

carboxylate group of the amino acids. The analytical data suggest a mononuclear structure for the complexes. All the oxovanadium (IV) complexes are found to show antifungal activity. Structural characterisation indicate square pyramidal geometry.

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